

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>4</sup> : C03C 13/00, 13/06, C04B 35/02 C04B 35/22		A1	(11) International Publication Number: WO 87/ 05007 (43) International Publication Date: 27 August 1987 (27.08.87)
(21) International Application Number: PCT/US87/00313		(74) Agent: QUINN, Cornelius, P.; Patent and Licensing Department, Manville Corporation, P.O. Box 5108, Denver, CO 80217-5108 (US).	
(22) International Filing Date: 17 February 1987 (17.02.87)			
(31) Priority Application Numbers: 831,217 894,175		(81) Designated States: AT (European patent), AU, BE (Eu- ropean patent), BR, CH (European patent), DE (Eu- ropean patent), DK, FI, FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent).	
(32) Priority Dates: 20 February 1986 (20.02.86) 7 August 1986 (07.08.86)			
(33) Priority Country: US			
(71) Applicant: MANVILLE CORPORATION [US/US]; Patent and Licensing Department, P.O. Box 5108, Denver, CO 80217-5108 (US).		Published With international search report.	
(72) Inventors: OLDS, Leonard, Elmo : 977 S. Lake Gulch Road, Castle Rock, CO 80104 (US). KIELMEYER, William, Henry : 3374 West Chenango Avenue, Eng- lewood, CO 80110 (US).			

(54) Title: INORGANIC FIBER COMPOSITION CONSISTING ESSENTIALLY OF  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$  AND  $\text{SiO}_2$ 

## (57) Abstract

Inorganic fiber compositions consisting essentially of  $\text{SiO}_2$ ,  $\text{CaO}$ , about 0.1-30 wt %  $\text{MgO}$ , and 0-10 wt %  $\text{Al}_2\text{O}_3$ . The fibers of this invention are suitable for thermal insulation at continuous service temperatures from 1370°F to 1500°F and find particular use as insulating mats and blankets for furnaces, kilns, and automobile catalytic converters.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT:

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland				

## INORGANIC FIBER COMPOSITION CONSISTING ESSENTIALLY OF

 $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$  AND  $\text{SiO}_2$ 

This application is a continuation-in-part of copending application Serial No. 831,217, filed February 20, 1986.

Field of the Invention

5           This invention relates to an inorganic fiber composition made from oxide melts. More particularly, it relates to an inorganic fiber composition made from silica, calcium oxide, magnesia and optionally, alumina.

Background of the Invention

10           For many years inorganic fibers, generically referred to in the industry as "mineral wool fibers", made from slag, rock, fly ash, and other by-product raw materials have been manufactured. These fibers have almost invariably had some degree of alumina content and have been typically manufactured by melting the slag, rock, etc., containing  
15           alumina and other oxides such as silica, allowing the molten material to be blown by gas or steam or to impinge on rotors at high speed and causing the resulting blown or spun fibers to be accumulated on a collecting surface. These fibers are then used in bulk or in the form of mats, blankets, and the like as high temperature insulation. However,  
20           whereas such mineral wool insulation products have had some degree of commercial acceptance they are not without some disadvantages.

          To begin with, the slag, rock, and other materials from which mineral wool fibers are commonly made may contain relatively high amounts of undesired oxides and other materials which not only do not  
25           impart any degree of refractoriness to the manufactured fiber, but in many instances actually detract from such. This also detrimentally affects the general fire resistance properties of the fiber. Additionally, since the slag, rocks, and other by-product raw materials are so highly variable in composition, it is very time consuming,  
30           laborious, and in many instances, virtually impossible to try to adequately control the metal oxide content of the manufactured fiber to within specified limits. Unfortunately, this means that mineral wool fibers used in bulk or in the form of mats, blankets, and the like offer  
          no real guarantee of a continuous service temperature. The foregoing  
35           cited problems with the manufacture and use of traditional mineral wool fibers signifies that improvements are needed.

05      What is needed in the industry is a relatively low cost and effective replacement for traditional mineral wool fibers. Specifically, a replacement fiber which is easy to make and control the composition of within strict limits and which offers a continuously high service temperature would be highly desirable. Fibers which also have good fire resistance properties are additionally highly desirable and sought after by those in the industry.

### Summary of the Invention

In accordance with the present invention, Applicants have developed an inorganic fiber which is an economical and effective substitute for traditional mineral wool fibers. Applicants' fiber has a composition consisting essentially of  $\text{SiO}_2$ ,  $\text{CaO}$ , about 0.1-30 wt %  $\text{MgO}$ , and about 0-10 wt %  $\text{Al}_2\text{O}_3$ . Applicants have discovered that not only does the inventive fiber have a continuously high service temperature, but also quite surprisingly has a superior solubility in some types of fluids.

10 In a preferred embodiment, the inventive fiber has a composition consisting essentially of  $\text{SiO}_2$ ,  $\text{CaO}$ , about 0.1-30 wt %  $\text{MgO}$ , and about 0-8 wt %  $\text{Al}_2\text{O}_3$ . These fibers have been found to have particularly good refractory properties.

In a preferred embodiment, the inventive fiber has a composition consisting essentially of about: 29-44 wt %  $\text{CaO}$ , 55-64 wt %  $\text{SiO}_2$ , 0.1-8 wt %  $\text{MgO}$ , and 0-4 wt %  $\text{Al}_2\text{O}_3$ . These fibers have particularly good fire resistance properties as well as good refractory properties.

By making the inventive fiber composition directly from a melt of metal oxides rather than raw by-product materials of widely varying composition which can contain relatively high amounts of materials other than the desired metal oxides, the foregoing problems associated with making and using traditional mineral wool fibers are eliminated.

Since the inventive fibers are made directly from the oxide form of the metals used, time consuming and laborious procedures are not needed to formulate a desired composition within a specified range. Furthermore, the inventive fibers will now have a continuous service temperature which guarantees their ability to be utilized in situations where such a continuous service temperature is needed. In fact, as shown later herein, the inventive fibers have a continuous service temperature of as high as 1500°F. Since the major undesired components of slag, rock, etc., previously found in traditional mineral wool fibers are not present in the inventive fibers, the latter have a high degree of refractoriness and thus can be utilized in the lower service temperature ranges of normal refractory fibers having a high alumina content which tends to make them relatively expensive.

These and other aspects as well as the several advantages of Applicants' invention are apparent from the specification and appended claims.

Detailed Description of the Invention

The invention herein comprises inorganic fiber compositions made from a melt consisting essentially of  $\text{SiO}_2$ , CaO, about 0.1-30 wt % MgO, and about 0-10 wt %  $\text{Al}_2\text{O}_3$ . In a preferred embodiment, the inventive fiber is made from a melt consisting essentially of  $\text{SiO}_2$ , CaO, about 0.1-30 wt % MgO, and about 0-8 wt %  $\text{Al}_2\text{O}_3$ . In another preferred embodiment, the inventive fiber is made from a melt consisting essentially of about: 29-44 wt % CaO, 55-64 wt %  $\text{SiO}_2$ , 0.1-8 wt % MgO, and about 0-4 wt %  $\text{Al}_2\text{O}_3$ . The fibers of the present invention have exhibited continuous service temperatures as high as in the range of about 1370°F to about 1500°F.

The metal oxides of the inventive composition are available in a relatively pure form from many commercial sources. Physical variables such as particle size may be chosen on the basis of cost, handleability, and similar considerations. Purity of the oxides used should be maintained at a relatively high level, such that no more than about 1% to 2% impurities in the form of other oxides, organic materials and the like are present in the finished fiber, since the presence of such impurities will have detrimental effects on the temperature rating of the fiber.

As used herein, the "service temperature" of fiber is determined by two parameters. The first is the obvious condition that the fiber must not melt or sinter at the temperature specified. It is this criterion which precludes the use of many of the glass and mineral wool fibers at temperatures above 1200°F (650°C). Second, a felt or blanket made from the fibers must not have excessive shrinkage at its service temperature. "Excessive shrinkage" is usually defined to be a maximum of 5% linear shrinkage after prolonged exposure (usually for 24 hours) at the service temperature. Shrinkage of mats or blankets used as furnace liners and the like is of course a critical feature, for when the mats or blankets shrink they open fissures between them through which the heat can flow, thus defeating the purpose of the insulation. Thus, a fiber rated as a "1500°F (815°C) fiber" would be defined as one which does not melt or sinter and which has acceptable shrinkage at that temperature, but which begins to suffer in one or more of the standard parameters at temperatures above 1500°F (815°C).

The fiber is formed in conventional inorganic fiber forming equipment and using standard inorganic fiber forming techniques. Normally production will be by electric furnace melting. The various raw materials are granulated to a size commonly used for fiber melt materials. or may be purchased already so granulated. The granulated raw materials are mixed together and fed to the electric furnace where they are melted by electrical resistance melting. Melt formation may be continuous- or batch-wise melting, although the former is much preferred. The molten mixture of oxides is then fed to fiber forming devices, such as spinners or blowers. A number of types of devices for fiber formation are well known and need not be described here. The fibers so formed will have lengths of 0.5 to 20 cm and diameters on the order of 0.5 to 10 microns with the average fiber diameter being about 1.5 to 3.5 microns. After fiberization the fibers may be collected in bulk or passed into separate devices intended to form the fibers into mats, blankets or similar structures. The techniques heretofore commonly used to form similar articles of high temperature alumino-silicate refractory fibers are quite suitable for use with the fibers of the present invention.

The following examples further illustrate the present invention.

#### EXAMPLE I

A series of inventive fibers were made according to the foregoing generalized procedure. Their respective compositions along with their service temperature ratings are given in Table I.

TABLE I

FIBER Components, wt %	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
	1450	1430	1400	1450	1400	1430	1390	1440	1400	1450	1370	1410	1380	1430	1380
Al <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0	0	0	0	5	5	7	8	8
SiO <sub>2</sub>	44	44	49	51	51	54	54	57	59	59	52	56	40	55	48
CaO	46	40	28	40	30	35	26	35	26	35	25	30	39	30	25
MgO	10	16	23	9	19	11	20	8	15	6	18	9	14	7	19
Service Temp.	1450	1430	1400	1450	1400	1430	1390	1440	1400	1450	1370	1410	1380	1430	1380
Rating °F	1450	1430	1400	1450	1400	1430	1390	1440	1400	1450	1370	1410	1380	1430	1380



The foregoing data clearly demonstrate that the inventive fibers would be very useful in higher temperature ranges, e.g. 1370°F to 1500°F, where it was either virtually impossible or very difficult to formulate the traditional mineral wool fibers that could be used in that range. It should be noted that fiber H was particularly fast melting and fiber L had particularly good fiberization properties.

#### EXAMPLE II

A series of fibers were made having the compositions given in Table II.

10 Each fiber was then tested for its fire resistance according to the following simulated fire rating test procedure:

For screening test purposes, a small furnace was constructed using an electrically heated flat-plate element at the back of the heat source. A 6 inch x 6 inch x 2 inch (thick) sample of 1-3/4 to 3 pcf density of each formulated fiber was mounted parallel with the element and 1 inch from it. Thermocouples were then positioned at the center of the fiber sample surfaces. A computer was used to control power via a simple on-off relay system to the heating element. The position of the relay was based on the reading of the thermocouple on the sample surface nearest the element and the programmed fire test heat-up schedule.

20 The furnace was heated so as to follow a standard ASTM E-119 time/temperature curve for a period of 1 hour and 2 hours respectively. In the test utilized herein, failure of the fiber is considered to occur when the furnace is unable to maintain the standard temperature per ASTM E-119 because the fiber insulation has sintered sufficiently to allow heat to escape through the furnace wall.

The test results for each fiber are given in Table II.

TABLE II

FIBER Components, wt %	A	B	C	D	E	F	G	H	I
10									
	<0.1	<0.1	<0.1	5.0	5.2	1.3	0.5	0.9	0.9
Al <sub>2</sub> O <sub>3</sub>									
SiO <sub>2</sub>	56.7	54.0	51.3	56.0	55.6	55.1	59.0	58.9	62.7
CaO	34.8	35.2	39.7	31.0	30.0	33.2	34.8	40.0	36.1
MgO	8.5	10.8	9.0	8.0	9.2	10.4	5.7	0.2	0.3
15									
Test Results*	F-1	F-1	F-1	F-1	F-1	F-1	P-2	P-2	P-2

\*P = Pass

F = Fail

1 = 1 hour fire rating test

20 2 = 2 hour fire rating test

The data in Table II show the clear fire resistance superiority of fibers G through I as compared to fibers A through F. Of special significance is the fact that these compositions attain their fire ratings at bulk densities and fiber diameters that are considerably lower than conventional mineral wool fibers. Fibers G through I attained the desired fire ratings with bulk densities of from 1-3/4 to 3 pcf and fiber diameters from 1-1/2 to 3-1/2 microns. In comparison, conventional mineral wool fibers attain their fire ratings with bulk densities typically of from 6 to 8 pcf and fiber diameters of from 4 to 6 microns.

Thus, the data clearly indicate that the preferred inventive fibers have surprisingly superior heat resistance properties.

#### EXAMPLE III

A series of fibers of varying formulations listed in Table III were tested for their solubility in a saline solution according to the following procedure: A buffered saline solution was prepared by adding to 6 liters of distilled water the following ingredients at the indicated concentrations:

	<u>Ingredient</u>	<u>Concentration, g/l</u>
20	MgCl <sub>2</sub> ·6H <sub>2</sub> O	0.160
	NaCl	6.171
	KCl	0.311
	Na <sub>2</sub> HPO <sub>4</sub>	0.149
	Na <sub>2</sub> SO <sub>4</sub>	0.079
25	CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.060
	NaHCO <sub>3</sub>	1.942
	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	1.066

One (1) gram of each sample of fiber listed in Table III was then placed into separate closed, plastic bottles along with 300 cc of the prepared saline solution and put into an ultrasonic bath for 5 hours. The ultrasonic vibration application was adjusted to give a temperature of 104°F at the end of the 5 hour period. At the end of the test period, each saline solution containing the fiber was chemically analyzed for SiO<sub>2</sub> content. The concentration SiO<sub>2</sub> in the saline solution was taken to be a measure of the amount of fiber which solubilized during the 5 hour test period. The continuous service temperature of each fiber was also measured. The results are given in Table III.

TABLE III

	FIBER	FIBER COMPOSITION WT %					SiO <sub>2</sub> CONCENTRATION IN SALINE SOLUTION AFTER 5 HOURS, WT %	CONTINUOUS SVC. TEMP °F*
		Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO	Misc.		
5	A	46	54	--	--	--	0.6	2400
	B	40	50	6	4	--	0.5	1600
	C	23	60	3	14	--	0.7	1390
	D	22	48	17	13	--	0.5	1380
	E	10.7	52	22	16	--	0.7	1370
10	F	10.2	52	21	15	--	0.5	1370
	G	8.9	52	22	16	--	1.2	1370
	H	8.7	52	22	16	--	1.7	1370
	I	8.0	56	30	7	--	5.1	1390
	J	9.1	40	37	11	2.6	7.7	1200
15	K	9.3	39	38	14	--	13.0	1380
	L	0	49	28	23	--	67.0	1380

\*Temperature for 3% maximum linear shrinkage in 24 hours.

The FIGURE graphically shows the relationship between the alumina content of each fiber and its silica extraction (i.e. solubility) in the prepared saline solution.

The FIGURE clearly shows that inventive fibers G-L which possess 10 wt % or less alumina clearly have a surprisingly higher solubility in the prepared saline solution than non-inventive fibers A-F which possess higher alumina contents. The surprising nature of Applicants' discovery is clearly apparent by the fact that there is a markedly noticeable difference in solubility between non-inventive fiber F as compared to inventive fiber G even though their difference in alumina content is relatively small (i.e. 10.2 wt % vs. 8.9 wt %).

The extremely high solubility of fiber L is particularly noted.

Reasonable variations and modifications of the foregoing are possible without departing from either the spirit or scope of the present invention.

We claim:

1. An inorganic fiber having a composition consisting essentially of about:

- (a) 0.1-30 wt % MgO;
- (b) 0-10 wt %  $\text{Al}_2\text{O}_3$ ;
- (c)  $\text{SiO}_2$ ; and
- (d) CaO.

2. An inorganic fiber according to claim 1 having a composition consisting essentially of about:

- (a) 0.1-30 wt % MgO;
- (b) 0-8 wt %  $\text{Al}_2\text{O}_3$ ;
- (c)  $\text{SiO}_2$ ; and
- (d) CaO.

3. An inorganic fiber according to Claim 1 having a composition consisting essentially of about:

- (a) 0.1-8 wt % MgO;
- (b) 0-4 wt %  $\text{Al}_2\text{O}_3$ ;
- (c) 55-64 wt %  $\text{SiO}_2$ ; and
- (d) 29-44 wt % CaO.

4. An inorganic fiber according to Claim 1 having shrinkage resistance of no greater than 5% when subjected to temperatures from 1370°F to 1500°F for about 24 hours.

5. An inorganic fiber according to Claim 2 having shrinkage resistance of no greater than 5% when subjected to temperatures from 1370°F to 1500°F for about 24 hours.

6. An inorganic fiber according to Claim 3 having shrinkage resistance of no greater than 5% when subjected to temperatures from 1370°F to 1500°F for about 24 hours.

7. A matted inorganic fiber body composed of a plurality of the fibers of the composition of Claim 1.

8. A matted inorganic fiber body composed of a plurality of the fibers of the composition of Claim 2.

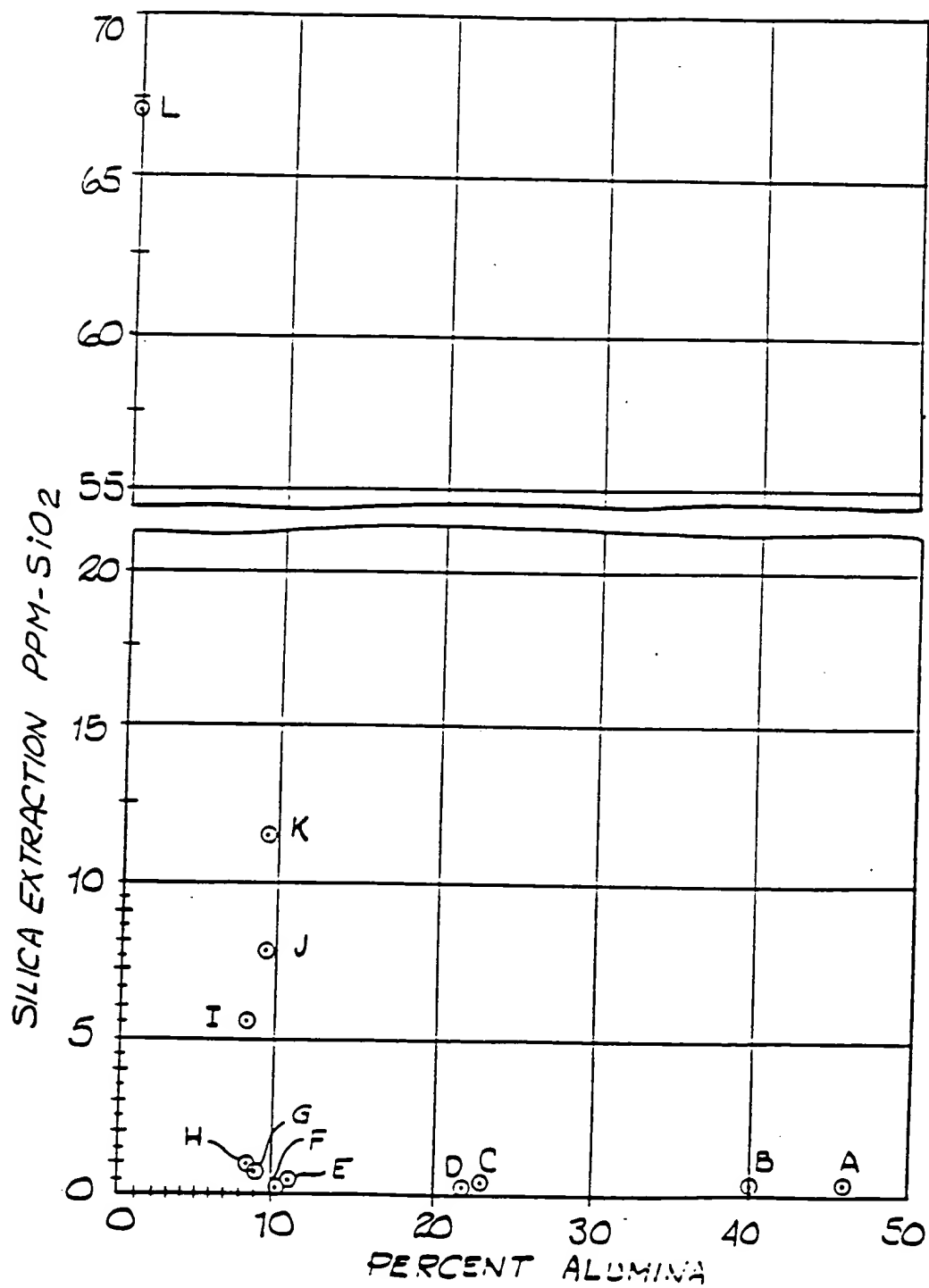
9. A matted inorganic fiber body composed of a plurality of the fibers of the composition of Claim 3.

10. An inorganic fiber having a composition consisting essentially of about

- (a) 0.1-30 wt %  $\text{MgO}$ ;
- (b) 0-10 wt %  $\text{Al}_2\text{O}_3$ ;
- (c)  $\text{SiO}_2$ ; and
- (d)  $\text{CaO}$ ;

and having a superior solubility in saline solutions.

1/1



# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US87/00313

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) <sup>1</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. <sup>4</sup> C03C 13/00, 13/06; C04B 35/02, 35/22

US. CL. 501/35, 36, 95

## II. FIELDS SEARCHED

Minimum Documentation Searched <sup>\*</sup>

Classification System

Classification Symbols

US 501/35, 36, 95

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>\*</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>1,2</sup>

Category <sup>*</sup>	Citation of Document, <sup>1,2</sup> with indication, where appropriate, of the relevant passages <sup>1,2</sup>	Relevant to Claim No. <sup>1,2</sup>
X Y	US, A, 2,576,312 (MINNICK) 27 November 1973, Column 1, lines 13-19 and claim 3.	1-6, 10, 7-9
X Y	SU, A, 607,807 (MOSC ENG CONS INST) 05 May 1978, See entire document.	1-6, 10 7-9
X Y	GB, A, 520,247 (NAAML00ZE UENNOOTSCHAP MAATSCHAPPIJ TOT BEHEER EN EXPLOITATIE VAN OCTROOIEN) 18 April 1940, Pages 2 and 3.	1-6, 10 7-9
X Y	AU, B, 255,803 (CULLEN) 04 July 1963, Page 2 last 4 lines; Page 3; Table on Page 6; Fig. 1 and 2.	1-6, 10 7-9

<sup>\*</sup> Special categories of cited documents: <sup>1,2</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search <sup>1</sup>

11 March 1987

International Searching Authority <sup>1</sup>

ISA/US

Date of Mailing of this International Search Report <sup>1</sup>

24 MAR 1987

Signature of Authorized Officer <sup>1,2</sup>

Mark Bell

*Mark Bell*